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SOLAR EVAPORATION SYSTEM: MODELING AND CONTROLLING BRINE TREATMENT PONDS

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March 2016

March 2016


Liquid water exists on Mars,
boosting hopes for life there -NASA
Run Mars...Run !!!
VIA 9GAG.COM
Save yourself

Agradecimentos/ Acknowledgements

Aos meus orientadores no CTM, Jordi Mácia e Mario Heredero que além de serem grandes pessoas se preocuparam em integrar-me e ajudar-me ao longo do projecto tornando-o "mais fácil". E também obrigada por tudo que aprendi e por terem tornado a estadia fora ainda melhor.

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Sumário

O planeta Terra está a sofrer um problema de escassez de água que pode ser causado por quatro diferentes causas: alterações climáticas, poluição, agricultura e crescimento populacional.

De maneira a tentar resolver este problema, várias técnicas foram estudadas e estão a ser melhoradas, mas a melhor aposta será a dessalinização da água do mar.

Existem vários processos de dessalinização: dessalinização térmica (dessalinização multi-flash, dessalinização multi efeito e compressão de vapor) e dessalinização por membranas (osmose inversa e electrodiálise).

O projecto em que esta tese é baseada chama-se Zelda: dessalinização com descarga zero.

No projecto Zelda, a água do mar é tratada por osmose inversa e electrodiálise metátese e um dos produtos finais, a salmoura, é sujeita a um tratamento por evaporação solar em dois tanques (um aberto e outro fechado com uma ventoínha).

Os tanques são estudados nesta tese e o objectivo é criar um modelo em Matlab que consiga prever o comportamento dos tanques no que diz respeito à transferência de calor e massa (avaliando o nível de água dos tanques) e avaliar se funcionam como previsto para se conseguir cumprir o objectivo do projecto Zelda: recuperar os sais e evitar a sua descarga outra vez nos oceanos, o que pode provocar impactes negativos no ecossitema.

Para criar este modelo foram escritos dois sub-modelos em Matlab, baseados num projecto designado por AQUASOL. Um dos sub-modelos é o mesmo que no projecto AQUASOL (Modelo 2) e o outro sub-modelo foi posteriormente desenvolvido pelo CTM de acordo com as restrinções e casos previstos (Modelo 1).

Após comparação dos dois sub-modelos e aquisição dos dados foi obtido um modelo final de modo a prever as transferências de calor e massa que ocorrem dentro dos tanques.

Palavras-chave: dessalinização, evaporação solar, transferência de calor.

Abstract

Our planet Earth is facing a water scarcity problem that can be caused by four different factors: climate changes, pollution, agriculture and population growth.

In order to solve this problem, many techniques have been developed and are being improved, but the best bet is seawater desalination.

There are many processes for water desalination: thermal desalination (multi flash distillation, multi effect distillation and vapor compression) and desalination by membranes (reverse osmosis and electrodialysis).

This thesis is about the final part of a project called Zelda: Zero Liquid Discharge Desalination.

In the Zelda project the seawater is treated by reverse osmosis and electrodialysis methatesis processes and one of the final products, the brine, is treated by a solar evaporation process in two ponds (one open and the other closed with a fan).

The ponds are the ones being studied in this thesis and the objective is to create a Matlab model that can predict the behaviour of the ponds in what concerns heat and mass transfer (assessing the water level in the ponds) and analyse if they work as expected in order to fullfill the main objective of the Zelda project: recover the salts and avoid their release back to the oceans, which can provoque negative impacts on the ecosystem.

In order to create this Matlab model, two sub-models were written, based on a project called AQUASOL. One of the models is the same as in the AQUASOL project, and the other one was developed by the CTM team and me with all the restritions and conditions of the ponds.

After comparation of both sub-models and data acquisition, a new final model was written in a way that the heat and mass transfers inside the ponds could be estimated.

Key words: desalination, solar evaporation, heat tranfer.

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Notation

ε – Emissivity (between 0 and 1)

σ – Stefan-Boltzmann constant, $W/m^2.K^4$

Be – Baumé scale, ºBe

C_{evap} – Evaporation coefficient depending on the brine saline concentration and referred to distilled after evaporation.

C_l – Vaporization latent heat.

Cp,brine – Heat capacity of the brine, J/K

d – Depth (m)

F_s – Fraction of the solar energy absorbed by the brine layer.

H_h – Global irradiation in the horizontal plane.

h – heat transfer coefficient, $W/m^2.ºC$

k – Thermal conductivity, W/m.ºC

K – Soil conductivity, W/m.ºC

l – Total thickness, m

$P_{s,Tbrine}$ – Saturation pressure at brine temperature, Pa

$P_{s,Tair}$ - Saturation pressure at air temperature, Pa

q_b – Conduction heat transfer, W/m^2

q_c – Convection heat transfer, W/m^2

q_e – Evaporation heat transfer, W/m^2

q_r – Radiation heat transfer, W/m^2

v – Air flow velocity, m/s

$\boldsymbol{\rho_{brine}}$ – Density of the brine, kg/m^3

Glossary

CGP - Carrier Gas Process

CTM – Centre Tecnologic de Manresa

ED – Electrodialysis

GHG – Green House Gases

GOR - Gain Output Ratio

HDH - Solar Humidification Dehumidification

MD - Membrane Ditillation

MSF - Multistage Flash Distillation

MED - Multi Effect Distillation

RO - Reverse Osmosis

VC – Vapor Compression

WFD – Water Framework Directive

WHO – World Health Organization

ZLD – Zero Liquid Discharge

1 Introduction

This is the year 2016, 21st century, and despite all the evolutions and developments, since many years ago we are still facing problems related to the base of all types of life in our planet Earth: water scarcity.

Water scarcity occurs when the existing resources are less than the needed to fulfill the demand. Attention should be paid to not confuse water scarcity with drought. Drought is when the availability of the resource (in this case water) decreases when, for example, it doesn't rain for a long period of time [1].

The surface of the earth is mostly constituted by water, about 97% is the ocean and the other 3% is fresh water in which about 1% is available for human use [2].

Water is always recycling, it's called the Water Cycle which is a process of water transfer through its many states and is responsible for the natural recharge of aquifers, lakes and rivers that are the main sources of water supply for human use. But still, it is a finite resource [2].

It is important to mention that the fresh water distribution isn't uniform and that's why the access is limited in some regions and abundant in others. Its availability varies from year to year and region to region [2].

In Figure 1 it's possible to see more specifically the earth's water distribution.

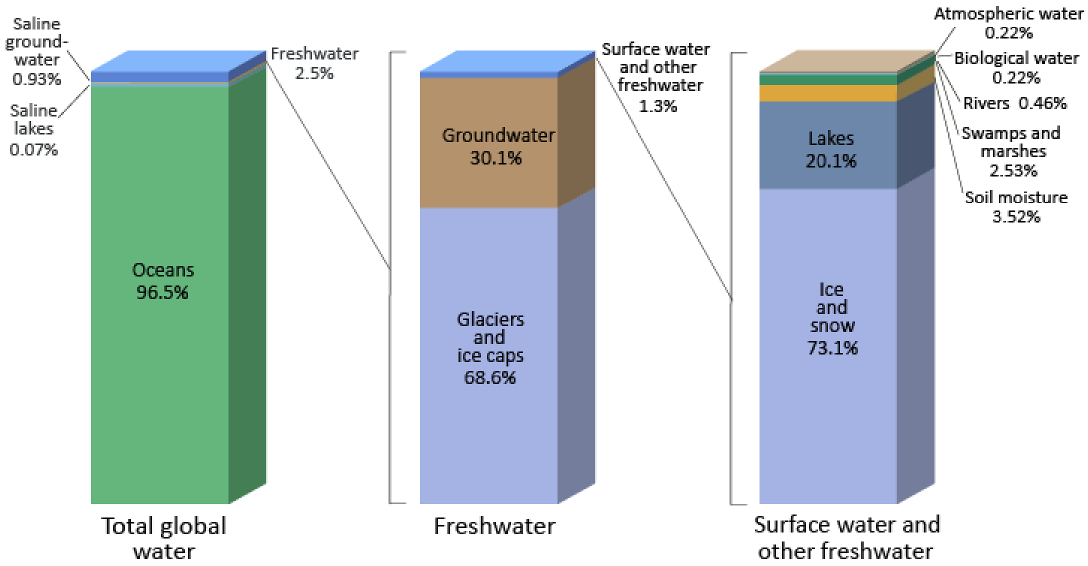

Figure 1: Distribution of Earth's Water [2].

Why are we facing water scarcity all over the world?

It is estimated that about 783 million people don't have access to freshwater, 2.5 billion don't have access to basic sanitation, more than 300 million from Africa suffer from water scarcity, 1.2 billion people live in scarcity areas and only 67% of the population have access to basic sanitation [2] [3].

In 2025 is expected that two thirds of the world population will be facing water shortages.

There are four main causes for water scarcity: climate changes, pollution, agriculture and population growth [4].

Climate changes are related to the emission of carbon dioxide (CO_2) and other greenhouse gases (GHG) to the atmosphere. These gases affect the weather and water conditions and as a result we have floods or droughts. One of the things that happens is the increase of the temperature that causes glaciers to disappear and affect the freshwater supplies [4].

With all of these changes there's less water available for agriculture, energy generation, cities and ecosystems [4].

Regarding the pollution, it comes in many ways, for example, from agriculture (pesticides and fertilizers that are washed away), untreated wastewater and also from industrial waste [4].

Agriculture uses 70% of the water available but about 60% of this 70% is waste because of many leaks or human mistakes [4] [5] [6].

India, China, Australia, Spain and USA are some countries that produce lots of food and are reaching their water resource limit [4].

The population growth affects the water scarcity because with this growth comes economic development and industrialization which causes water ecosystems transformations and loss of biodiversity [4].

Over the years the population has been facing the process of urbanization that means that there is an increase of the population and there are technological and industrial developments. With this increase and developments the amount of water needed and the production of waste increases and we started to use more than we have. It's possible to say that the people are not taking care of our limited resources and they are making a fast consumption of natural resources.

Despite of this consumption people also "ruin" water resources with other actions like: introducing toxic materials in the fresh water and residues from water treatment techniques. They also affect the water quality by untreated sewage, not controlling industrial effluents, destroying basins and not controlling the agriculture consumption [3].

Brown and Matlock quoted Falkenmark saying that the freshwater scarcity is function of available water resources and human population as illustrated in Table 1 [7].

Table 1: Conditions of freshwater scarcity according to Falkenmark [7].

Water avaiability (m^3 per capita/ year)	Condition
> 1700	No stress
1000 – 1700	Stress
500 – 1000	Scarcity
< 500	Absolute Scarcity

Brown and Matlock also quoted Gleick that wrote about minimum requirements regarding the consumption of freshwater as can be evaluated in Table 2 [7].

Table 2: Requirements of water consumption according to Gleick [7].

Requirement	L / person/ day
Minimum drinking water	5
Basic for sanitation	20
Basic for bathing	15
Basic for food preparation	10

There is a way to evaluate the freshwater consumption by a tool called the Water Footprint. This tool can indicate the volume of freshwater that is consumed by a country, organization, person, product or activity [8].

The Water Footprint of a product can be defined as the total volume of freshwater that is used from the "cradle to the grave" (i.e., since the extraction of raw materials until the product production) and there are three different footprints: green (consumption of stored rain water in the soil as humidity, and in the surface of the vegetation), blue (surface or underground water consumption) and grey (indicator of polluted water as a result of human activities) [8].

There are many techniques for water treatment to produce potable water but depending on which one they come with a high cost and are very complex. Other techniques use freshwater with the minimum conditions to be treated and then to be used.

For all those reasons presented for water scarcity and because of the fact that 97% of the planet Earth is the ocean, desalination techniques started to be used.

In the last decades desalination processes are being studied to produce potable water for the many uses that is needed. These processes basically turn salty water to freshwater.

1.1 Zelda project

As written before, through the last decades there was na improvement in the desalination techniques that can turn seawater into potable water in regions facing water scarcity. Despite the fact that these tchnologies have a socio-economic positive impact they also can cause problems to the environment.

Many of these technologies use membranes to separate the water from the dissolved salts in the seawater, so the result is a highly saline solution (brine). What happens to the brine? Is returned to the ocean and causes a negative impact to the marine ecosystem: destroying marine ecosystems, diminishing the amount of flora and create salinity, promoting also temperature and alkalinity gradients.

This thesis is about what happens to the brine obtained after the seawater desalination treatment. Zelda stands for Zero Liquid Discharge Desalination and there's a brine treatment based on a combination of electro-separation processes and valuable compound recovery [9].

Basically the seawater suffers two different desalination treatments (reverse osmosis and electrodialysis metathesis) and then the brine goes to solar evaporation ponds to further treatment with the objective to return the salts, to avoid their release back to the oceans and negative impact on the environment.

There are two ponds, one covered (that can be called ''forced'' because it suffers from forced convection) and one uncovered (natural), and the objective is to obtained a perfect model explaining the evaporation in each pond (Model 3).

Increasing the water recovery of the existing desalination plants, decreasing the brine discharge to water bodies and increasing the public awareness on the environmental impact of current brine discharge strategies, are some of the objectives of the Zelda project [9].

Some of the brine discharge strategies are: direct dischare, deep well injection, discharge to a wastewater facility and zero liquid discharge [33].

The main objective of the whole project is to compare environmental and economical impacts of the new process, with conventional brine management strategies by means of a life cycle analysis [9].

In Annex III there's a full description of the project.

2 Desalination Processes

Desalination in basically a process involving the conversion of salty water into potable water for human consum and human activities, like agriculture, energy production or colling systems [10].

Desalination can be made by several processes. Among them there is the thermal desalination by distillation that includes Multistage Flash Distillation (MSF), Multi Effect Distillation (MED) and Vapor Compression (VC) [10] [11].

The thermal desalination principals are: vapor formation by heat, separation of vapor from the seawater and condensation of the vapor [10] [11].

Desalination can also be carried out by membrane processes like: Reverse Osmosis (RO) and Electrodialysis (ED). These two types are the main technologies used but there are also other processes like: Membrane Distillation (MD), Solar Humidification Dehumidification (HDH) and Carrier Gas Process (CGP) [10] [11].

In the next chapters the thermal desalination processes will be explained along with the RO and ED among the membrane processes.

2.1 Reverse Osmosis (RO)

Reverse osmosis in a simple way is the separation of a solvent from a solute through a semipermeable membrane which is permeable to the solvent and impermeable to the solut. This process has both commercial and industrial applications: water treatment (namely in the production of pulp and paper), product recovery from wastewaters and ultrapure water production for hemodialysis [11] [12] [13].

A high power pump makes a big pressure on the mixture reversing the way of the natural flow. The membrane retains salts and harmful components to the human health. The pressure on the concentrate side is bigger than the osmotic pressure and there is a flow of clean water until the balance is achieved [11] [12] [13].

In figure 2 and 3 are illustrated the reverse osmosis concept and is provided the scheme of a process including a RO unit, respectively.

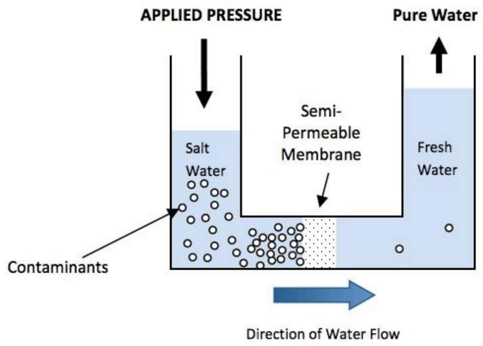

Figure 2: Reverse osmosis [14].

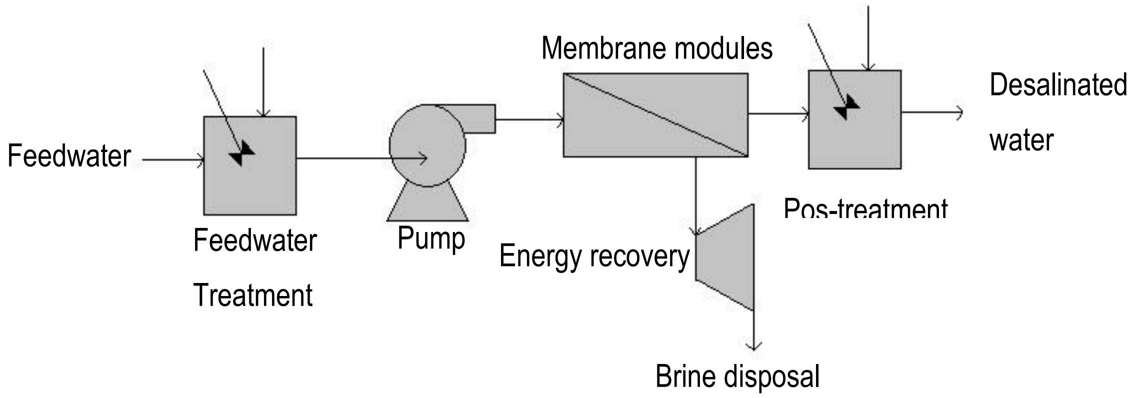

Figure 3: Scheme of a reverse osmosis installation [13].

In Table 3 and Table 4 are explained some of the benefits and disadvantages of the reverse osmosis process, respectively.

Table 3: Advantages of the RO treatment for desalination [12] [13].

Advantages
Low investment cost and energy consumption
The quality of the produced water is constant
The rejection rate of the rejected part can achieve 20-70%
Low maintenance
Can make use of an almost unlimited and reliable water source, the sea
Can be used to remove organic and inorganic contaminants
Has a negligible environmental impact
Minimal use of chemicals

Table 4: Disadvantages of Reverse Osmosis treatment for desalination [12] [13].

Disadvantages
Membranes are sensitive
The feed water usually needs to be pretreated to remove particulates (in order to prolong membrane life)
Requires a high quality standard for materials and equipment
Require a reliable energy source
Brine must be carefully disposed off to avoid negative environmental imapacts

2.2 Multistage Flash Distillation (MSF)

MSF is a process with several stages and has three main sections: heat input, heat recovery and heat rejection. In Figure 4 is illustrated an example of this process.

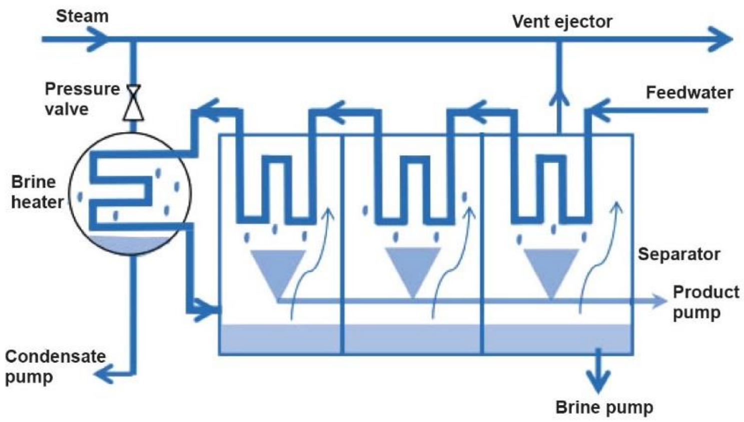

Figure 4: Multistage flash distillation [15].

Basically the seawater is firstly heated to its maximum temperature, in the brine heater, through an external heat vapor. The vapor pressure is controlled so that the brine can enter the stages with the proper pressure and temperature to occur the evaporation [13] [16].

The feed enters the first stage and the flashing occurs because of the vapor production from the steam release, until the temperature of the water is in thermodynamic equilibrium with the vapor pressure [16] [17].

The water continues to pass the stages and in each stage the brine temperature decreases proportionally to the steam produced and the concentration of salt increases [16] [17].

In Table 5 are listed a few advantages and disadvantages about this desalination process.

Table 5: Advantages and Disadvantages of the MSF process [18].

Advantages	Disadvantages
Low operating cost when waste heat is used	High operating costs when waste heat is not available
Quality of the feed water is not as important as for a reverse osmosis system	Requires both thermal and mechanical energy
High GOR - Gain Output Ratio	Operates at high temperatures that increase corrosion and scale formation
Adding stages improves efficiency and increases water production	Adding stages increases costs and operational complexity

2.3 Multi Effect Distillation (MED)

In a MED process there are many stages and several consecutive horizontal cells in which the first one is hot and the last one is cold [13] [18].

The steam is condensed in one side of the pipes and the sea water is evaporated on the other side; the energy used in this evaporation comes from the heat generated by the steam condensation [13] [18].

Each stage uses the energy produced in the one before and part of the brine evaporates while the other part follows to the next stage where gets heated and evaporates again. In the last stage the brine is pumped out since the pressure is lower than the atmosphere pressure [13] [18].

This process operates with low temperature and pressure, which prevents corrosion, and is very economical because it can be use aluminum or other kind of materials that are cheap. Moreover, the sea water doesn't need pre-treatment, so it's easy to operate and has a low maintenance cost [13] [18].

Other benefits about MED process are the following:

- Low energy consumption compared to other thermal processes;
- Can work all day, everyday with minimum supervision;
- Can be adapted to any heat source, including hot water, waste heat from power generation, industrial processes, or solar heating;

An example of MED is shown in Figure 5.

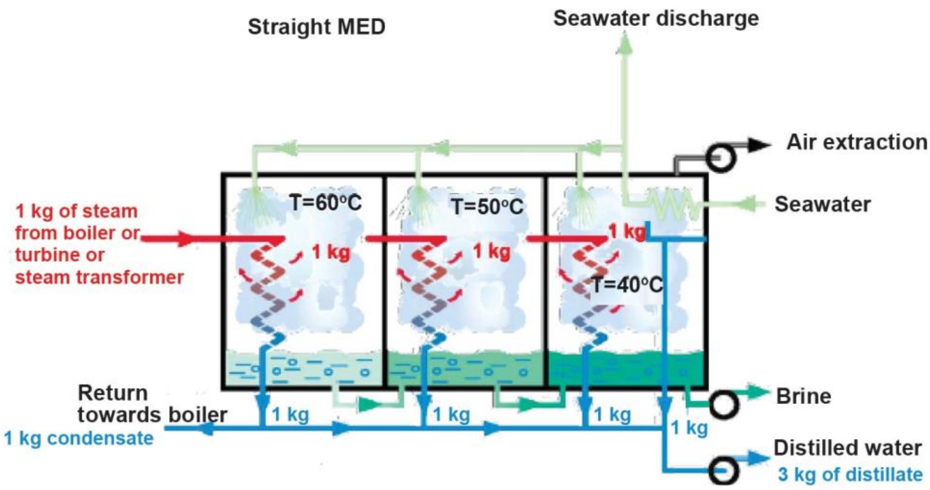

Figure 5: Multi-effect distillation *system* example [19].

2.4 Vapor Compression (VC)

In this process (VC) the water evaporation is caused by vacuum inside the evaporation chamber, which is caused by a mechanical compressor that can work by electric motor or a steam injector.

The evaporation produces a vapor that will be compressed and becomes the heat source to evaporate the feed water.

The tubes contain salty water and the pressurized vapor enters them condensating on the outside part of the tubes and also heating the salt inside the tubes [13] [18].

This last part of the process also produces water vapor which will be compressed again so the cycle will continue to produce condensed water as a product [13] [18].

In figure 6 is represented an example of this kind of process.

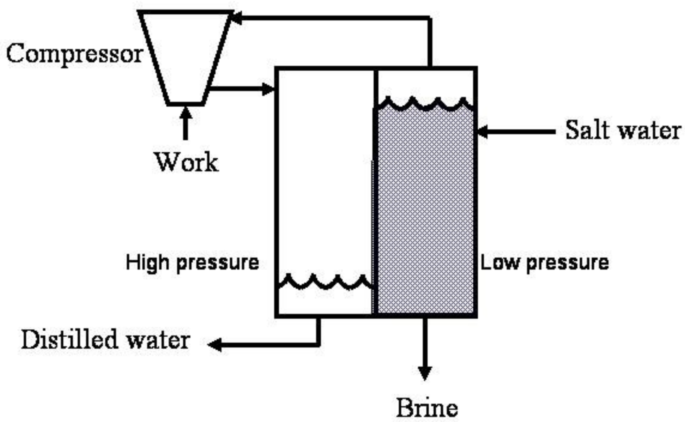

Figure 6: Example of Vapor Compression Technique [20].

In Table 6 are described a few advantages and disadvantages of the vapor compression process.

Table 6: Advantages and disadvantages regarding the VC process [21].

Advantages	Disadvantages
Operating costs lower than MSF and MED	Maintenance on compressors and heat exchangers
Equipment is smaller than the MSF and MED	High energy consumption
	High costs

2.5 Electrodialysis (ED)

Electrodialysis is a process that separates ions by using membranes permeable only to positive ions and other membranes only permeable to negative ones that are intercalated [22].

The ions start to migrate through the membranes when is added an electrical current to the water that is going to be desalinated [22].

There are many advantages related with this technique like the fact that it doesn't need high investments costs or special operational people.

Some other benefits about his process are listed next [22]:

- Can operate with minimal fouling or scaling, or chemical addition;
- Low pressure requirements;
- Installations are "quieter" than RO installations;
- Membranes have a long life;
- In feed water pretreatment are used few chemicals.

The low efficiency to highly concentrated salty water and the need of a pre-treatment of the water are some of the disadvantages of this technique [22].

In Figure 7 there is an example of the ED process.

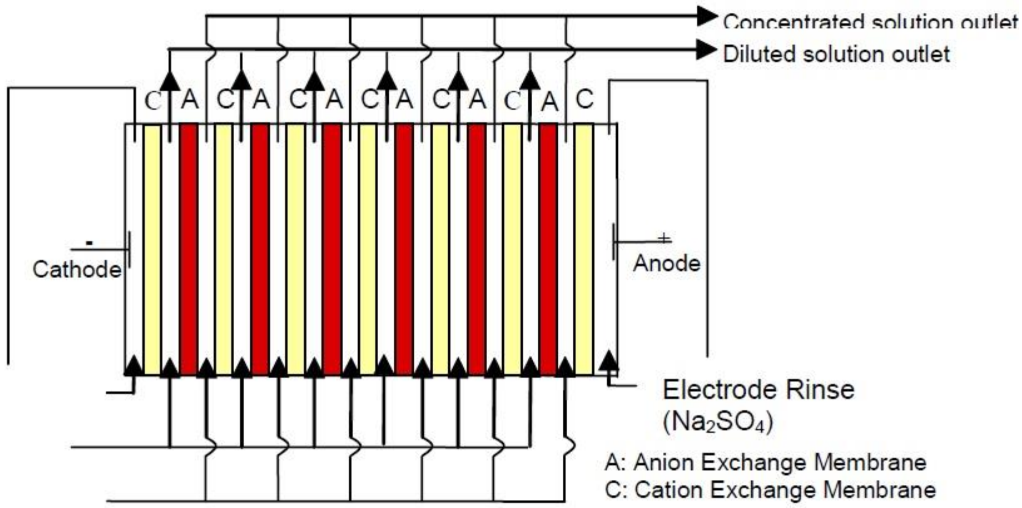

Figure 7: Electrodialysis process [23].

2.6 Comparing the processes

After presenting the most important desalination processses used all over the world, in this section is presented a comparision among them about several aspects.

In Table 7 is represented a comparison among the various processes according to heat and electrical energy costs.

Table 7: Costs for the main desalination processes [13].

Process	Heat energy (kWh/m^3)	Electrical Energy (kWh/m^3)
MED	63.8	1.6
MSF	81.2	3
VC	0	8.7
RO	0	3.5

After analysing Table 7 the conclusion is that the process that uses the most heat energy is MSF and in second is the MED process. Regarding the electrical energy, the processes that use more are the VC firstly and then the RO process.

In Table 8 we are able to see the costs related to the energy, labor, chemical products and maintenance.

Table 8: Global costs for the main desalination processes in euro/m^3 of potable water produced [13].

		MSF	MED	VC	RO
Energy	**Fuel**	0.40	0.30	-	-
	Electricity	0.20	0.11	0.60	0.25
Labor		0.04	0.04	0.07	0.07
Chemical products		0.05	0.04	0.04	0.05
Replacement of membranes		0.00	0.00	0.00	0.02
Maintenance		0.03	0.03	0.02	0.03
Total		**0.72**	**0.52**	**0.73**	**0.42**

Regarding the total costs of each process the more expensive ones are the MSF and the VC. This cost is big because of the energy necessary to make the process work.

The process less costly is the reverse osmosis with 0.42 €/m^3.

In Table 9 is represented a comparasion of the size of the plants with the costs for each process.

Table 9: Comparing sizes of plants with costs for several processes [24].

Processes	Size of plant (m^3/day)	Cost (€/per m^3)
MED	< 100	2.00 – 8.00
	12 000 – 55 000	0.76 – 1.56
	> 91 000	0.42 – 0.81
MSF	23 000 – 528 000	0.42 – 1.40
VC	1 000 – 1 200	1.61 – 2.13

After analysing Table 9 we can see that bigger the size of the plant for the MED process the lowest is the cost.

2.7 Plants in the world, main companies

2.7.1 Arab States of the Gulf (GCC)

The Arab States of the Gulf (GCC) include: United Arab Emirates (UAE), Kingdom of Bahrain, Kingdom of Saudi Arabia (KSA), Sultanate of Oman, State of Qatar and State of Kuwait.

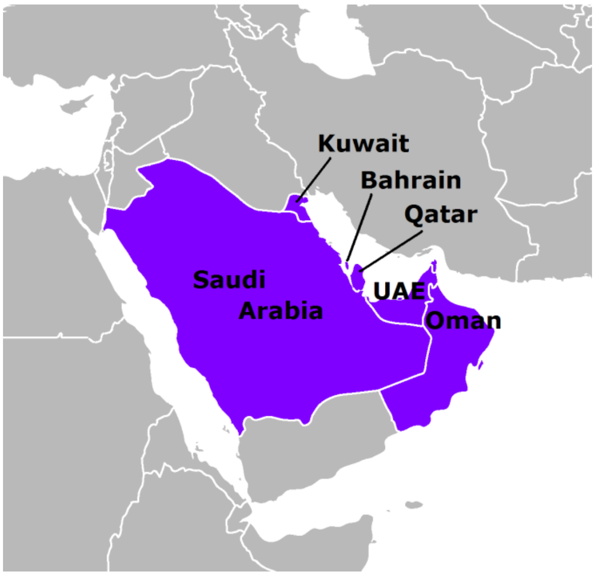

Figure 8: Map of the Arab States of the Gulf [25].

The GCC are located in the south west of the Asian continent. This part of Asia is considered an arid/semi-arid region that suffers from water scarcity and its primary source for freshwater is the groundwater [26].

These countries have been living several developments in the economical, industrial and agricultural areas. With these developments came the population growth and the increasing of demand related to freshwater.

Where the groundwater is not the primary source for freshwater, people depend on desalination processes as the main source of drinking water, so the GCC are concerned with looking for more effective, demanding less energy and less expensive processes.

The first use of reverse osmosis process in the GCC countries was in the KSA in 1968. Later on in 1987, 13 RO plants were built in Kuwait with the capacity of 1196 m^3/day and then, in 1993, were built 20 more plants [26].

UAE was the first to introduce the MED process with a plant with 91 m^3/day of capacity. Then, in 1981 they built two more units with the capacity of 825 m^3/day and then 9 plants with the total capacity of 227 273 m^3/day [26].

In 2008 the total desalination capacity was about 14.84 million m^3/day.

In Figures 9 and 10 is represented the contribution of each state and each process, respectively, for that total capacity.

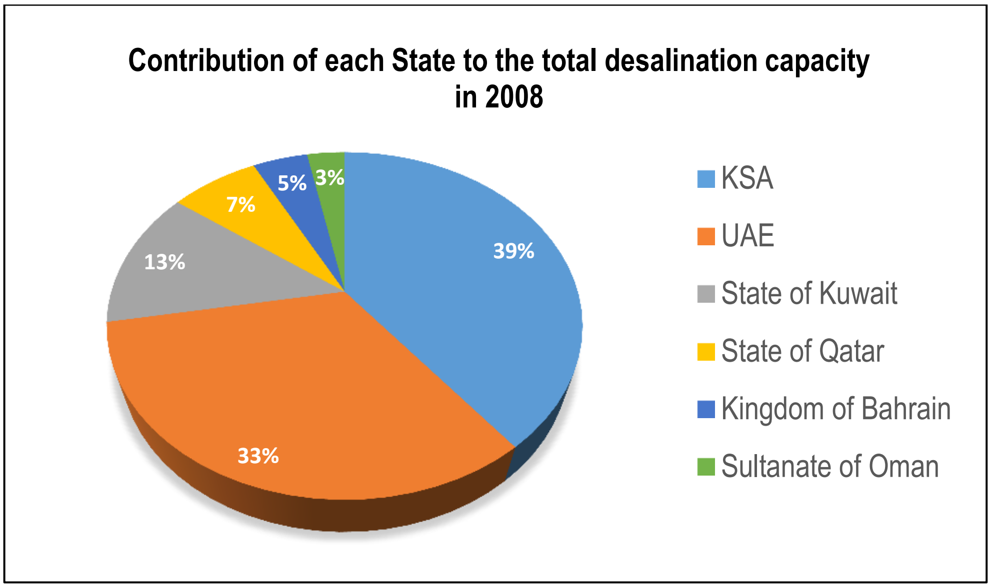

Figure 9: Contribution of each State to the total desalination capacity in 2008 in the GCC [26].

Analyzing Figure 9 is possible to observe that the Kingdom of Saudi Arabia has a more direct bearing in the total desalination capacity and the Sultanate of Oman has a less one.

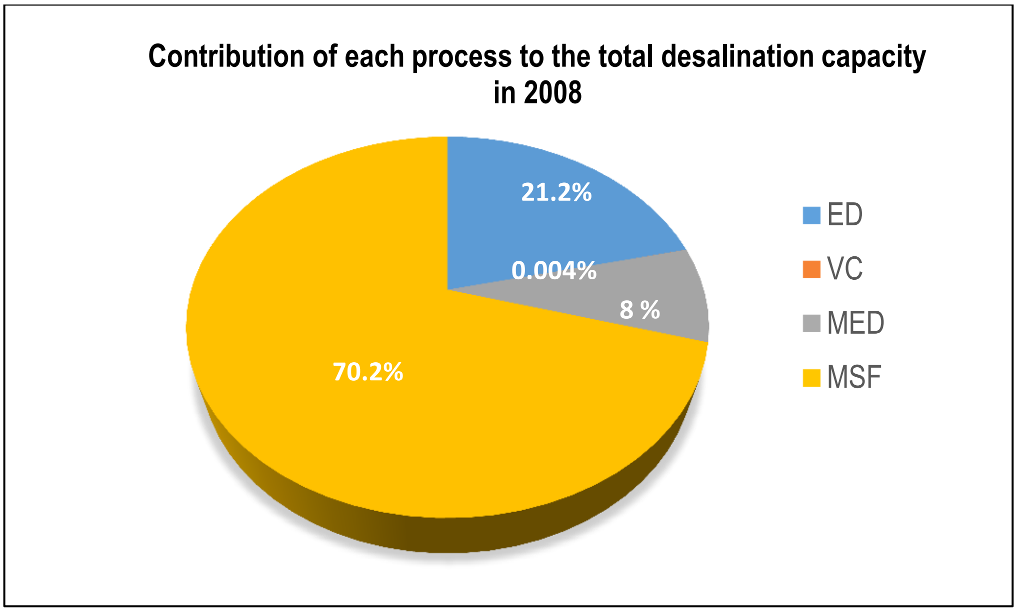

Figure 10: Contribution of each process to the total desalination capacity in 2008 in the GCC [26].

From Figure 10 it's possible to see that the process with more influence is the MSF process and the less used is the VC.

In Table 10 are shown the installed units and the indication of which distillation or destilation process is used in the GCC countries along with their capacities [26].

Table 10: Distillation and desalination processes and their capacity in the GCC countries [26].

<table>
<tr><th>Local</th><th>Date</th><th>Process type</th><th>Total capacity (m³/day)</th></tr>
<tr><td>State of Kwait</td><td>1960</td><td>MSF / Recycle (2 units)</td><td>9091</td></tr>
<tr><td>State of Qatar</td><td>1962</td><td>MSF / Long tubes</td><td>6818</td></tr>
<tr><td rowspan="2">Kingdom of South Arabia</td><td rowspan="2">1967</td><td rowspan="2">MSF / Once trough</td><td>198</td></tr>
<tr><td>198</td></tr>
<tr><td>State of Qatar</td><td>1968</td><td>MSF (2 units)</td><td>9000</td></tr>
<tr><td>Kingdom of Bahrain</td><td>1975</td><td>MSF / Recycle</td><td>22728</td></tr>
<tr><td rowspan="2">Sultunate of Oman</td><td rowspan="2">1976</td><td rowspan="2">MSF / Recycle</td><td>22728</td></tr>
<tr><td>15</td></tr>
<tr><td rowspan="3">United Arab Emirates</td><td rowspan="3">1977</td><td>MED</td><td>91</td></tr>
<tr><td>MSF / Recycle</td><td>68183</td></tr>
<tr><td>RO</td><td>4545.5</td></tr>
<tr><td>Sultunate of Oman</td><td>1979</td><td>VC</td><td>100</td></tr>
<tr><td>Sultunate of Oman and State of Qatar</td><td>1982</td><td>RO</td><td>100</td></tr>
<tr><td>Sultunate of Oman</td><td>1983</td><td>ED</td><td>100</td></tr>
<tr><td rowspan="2">Kingdom of Bahrain</td><td>1984</td><td>RO</td><td>4545.5</td></tr>
<tr><td>1985</td><td>VC</td><td>144</td></tr>
<tr><td>State of Qatar</td><td>1996</td><td>MED</td><td>9091</td></tr>
<tr><td>Kingdom of Bahrain</td><td>2004</td><td>MED</td><td>31818</td></tr>
</table>

3 The Zelda project description

The project entitled Zelda, despite of aiming to solve the world's water scarcity, also cares about the brine produced and its final destination as mentioned in chapter 1.

Many companies are involved in Zelda project: CTM, Fujifilm, Albengoa and the European Water Supply and Sanitation Technology Platform.

The final objective of the Zelda project is a zero liquid discharge (ZLD), which means that the concentrate is treated to produce water and there is no discharge of liquid waste from the process.

In fact, the destination of the brine produced during water desalination is a problem because normally the final destination of the brine is the sea where it is diluted again in its natural medium. However the brine isn't only salty waste. When the feed water enters the treatment processes, chemicals can be added, so that in the end they are sent to the ocean along with the brine. When sent to the ocean they can cause several damages such us destroying marine ecosystems, diminishing the amount of flora and create salinity, promoting also temperature and alkalinity gradients [28].

The Zelda project has duration of 4 years and this thesis is about the task related with the demonstration of the technology in a real desalination plant located in Almeria for seawater desalination.

In Zelda Project it's used the electrodialysis metathesis (EDM) for the brine desalination, after RO, and valuable compound recovery processes are implemented to prove the technical viability and economical sustainability in decreasing the global impacts caused by the desalination systems used to produce potable water.

The main objectives are concerned mainly with versatile brine treatment, performance and operational costs assessement, analysis ofthe influence of the brine composition and operating conditions of the EDM-ZLD system on the overall sustainability of the desalination process.

Decrease the discharge into the ocean, increase water recovering, reduce the environmental impact and grow the public concerns on the environmental impact of current brine discharge strategies are also objectives from the Zelda project.

3.1 Pilot plant: Almeria

The pilot plant is where the solar evaporation treatment is applied after the RO and the EDM treatments and consists in two ponds, one covered (forced air convection) and the other one uncovered (natural), to compare both natural and advanced evaporation as shown below in Figure 13.

It's located in Almeria, south of Spain, and the objective is to evaporate the water from the brine plus drying to obtain salt.

3.2 Electrodialysis metathesis (EDM)

In the Zelda project is used an EDM process, after the RO, that we can call an improvement of the ED process. Comparing with the ED process the main difference (but isn't the only one) is the number of compartments of membranes that are used.

This process is used to remove ions from water and the objective is to maximize the water production and the salt recovery.

EDM is implemented with four cells and four membranes that yield: one dilute and two concentrate compartments, a Sodium Chloride (NaCl) compartment, one anion and one cation exchange membrane, one monovalent selective anion and another one for cation membranes. The desalination concentrate from the reverse osmosis process is fed to the process and after applying a certain voltage the cations start to move to the right and the anions to the left as shown in Figure 11 [27].

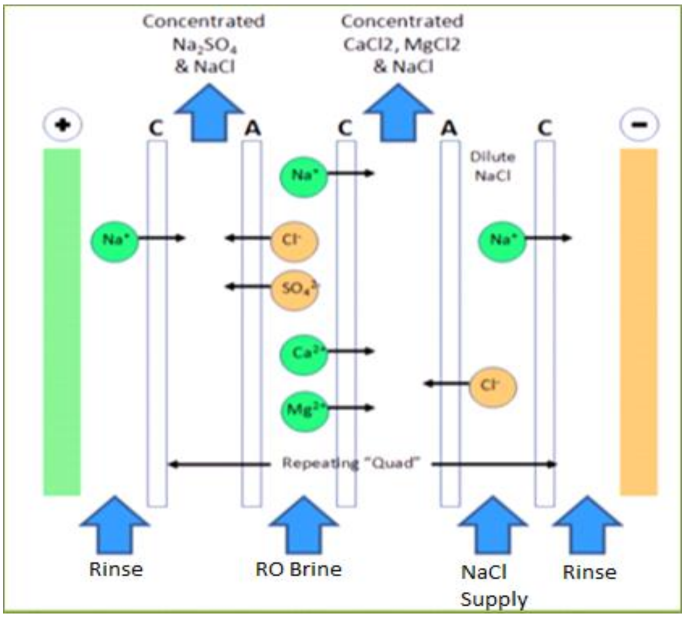

Figure 11: Electrodialysis metathesis process used in Zelda project [28].

When combined with the NaCl, the cation forms a chloride salt concentrate stream and the anions form a sodium salt concentrate stream. Then, these salt streams contain not so soluble compounds like: Calcium Chloride ($CaCl_2$) and Sodium Sulfate (Na_2SO_4). The sparingly soluble salts such as Calcium Sulfate ($CaSO_4$), Magnesium Sulfate ($MgSO_4$) or Calcium Carbonate ($CaCO_3$), are not produced in neither of the concentrate streams [27].

This unique configuration is designed to separate EDM concentrate into two streams of highly soluble salts: one containing sodium with anions and the other containing chloride with cations. This characteristic of EDM provides a significant advantage in treating RO concentrates because the membrane-fouling potentials of typical scalants such as $CaSO_4$ and $CaCO_3$ do not increase with recovery, as is the case with RO, nanofiltration, and other forms of electrodialysis, such as electrodialysis reversal (EDR) [27].

There are also other applications for this process: food processing, glycerin purification, capacitor electrolyte fluids, oil and gas dehydration, conditioning and processing solutions [27].

The advantages of this process are the fact that it is an improvement of the ED process and when compared with the RO the water recovery is higher. Previous work has shown that it is possible to recover up to 98% of the water from RO concentrate with EDM and the streams are highly concentrated facilitating the recovery of salts [27].

But it also has disadvantages like the fact that is a bit expensive and is needed someone with skills to work with it [27].

In Figure 12 is provided a scheme illustrating how the membrane process works.

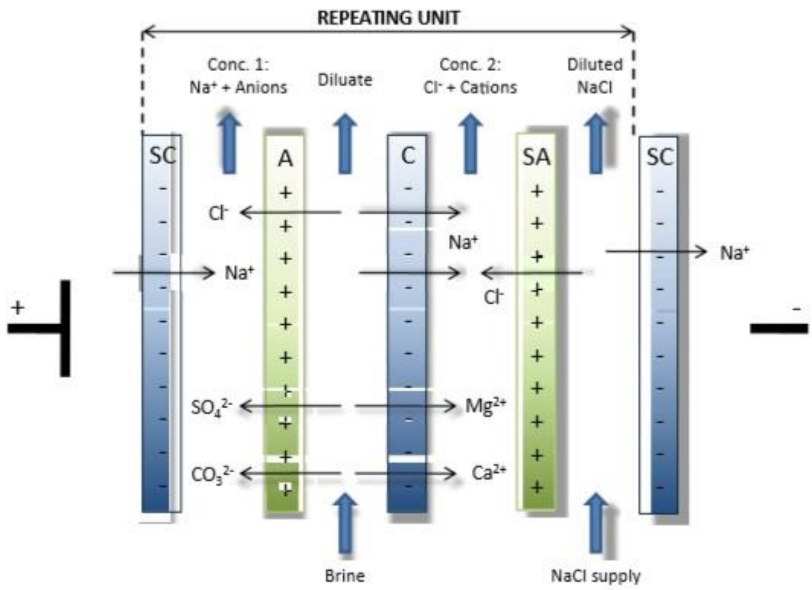

Figure 12: Interior of the membranes in the EDM [28].

The characteristics of the EDM plant are summarized in Table 11.

Table 11: Main characteristics of the EDM pilot plant [28].

Capacity of RO brine feed	0.5 - 1.5	m^3/h
Minimum brine production capacity	25 - 100	L/h
Maximum voltage total stack	300	V
Maximum current	50	A
Max. allowed temperature range of stack	10 - 40	°C
Expected temperature range inside the container	-5 - 50	°C
Expected temperature range outsider the container	0 - 45	°C
Internal leakage stack	< 0.5	mL/min.cell
Feed RO TDS range	3 - 60	g/L
Feed NaCl TDS range	5 - 100	g/L
Output diluate streams (D1 and D2)	0.02 - 6	g/L
Output concentrate streams (C1 and C2)	30 - 120	g/L

3.3 Advanced solar evaporation plant description

Evaporation ponds is where the brine is evaporated while the salts accumulate in the base of the pond. This kind of ponds had been used only for salt production but it has been proved that they work for brine disposal as well [29].

One of the problems is that the brine can leak through the pond so they should have liners to prevent that from happening and their depth should be controlled to prevent the liners from drying and cracking [29].

As described in Chapter 3.1 there are two ponds in Almeria's pilot plant: the covered one is made by fiberglass and vinyl ester resin and is covered by polycarbonate plates supported by a structure. It also has a system to control the ventilation and a control system of indoor air and a filling control.

The other pond, the uncovered one, is made by a composite material (fiberglass and vinyl ester resin) to evaluate natural evaporation on exposed rafts and its comparison with the controlled raft (forced convction pond) is aimed [28].

A storage tank of brine and filling system is where the effluent will be stored for the correct dosage of the brine into the ponds. This tank is placed on an elevated structure, so that the brine flows into the ponds with the operation of two solenoid valves (one per pond).

There's also a monitoring and control system that will allow monitoring the plant, makes the acquisition of operating data, storage and shipping via 3G connection (controller: Barebone PC (mini PC) con Windows OS y MATLAB, in and out exits: PCI o USB cards compatible with MATLAB® Data Acquisition Tool-box™ and IP camera)

This system has the objective of acquisition and registering the data, sending the data by 3G connection, control the level of liquid and drying and control the ventilation. In Annex I is possible to see the computer controller screen image [28].

The data obtained by the monitoring system is from the outside conditions (temperature, humidity and solar radiation), from the covered pond (temperature at the beginning and end, humidity at the beginning and end, temperature of the brine, velocity of the wind in the middle of the pond and ponds level) and from the uncovered pond (temperature of the brine, velocity and level) [28].

A scheme of the ponds is shown in Figure 13.

It is important to add the fact that the covered pond has an area to recover the condensated water and the dome has windows on the side that can be open as shown in Figure 13.

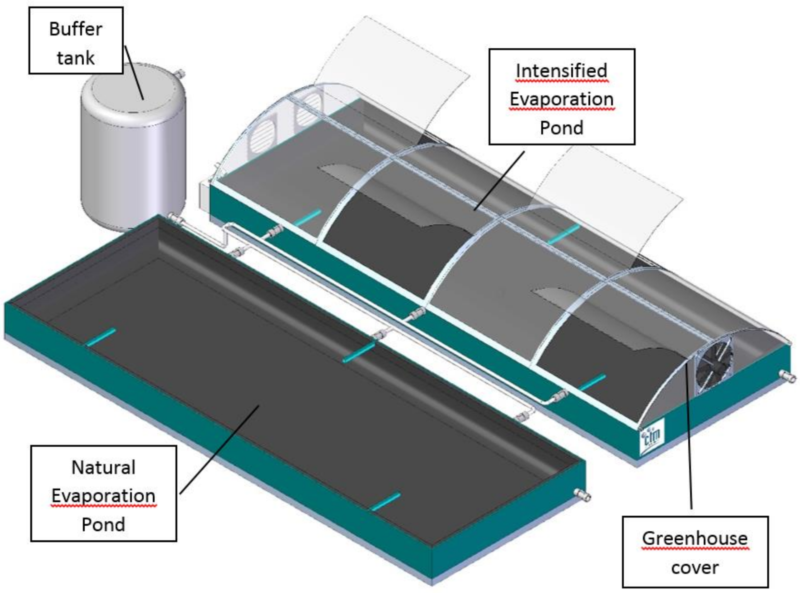

Figure 13: Evaporation ponds (uncovered and covered) [28].

In ANNEX I there is a photograph of the remote access to the ponds screen from where everyday data was collected and temperatures, levels, water flow, air renewal and humidity were recorded.
In Table 12 are demonstrated the specifications of the pilot plant in Almeria regarding the estimated performance for the natural and forced systems, the ponds surface area, the evaporation surface and the total plant capacity.

Table 12: Specifications for the pilot plant [28].

Advanced evaporation estimated performance	2 m^3/m^2.year
Natural evaporation estimated performance	1.2 m^3/m^2.year
Pond surface	8.3 m × 3 m = 25 m^2
Total evaporation surface	50 m^2
Total plant capacity	80 m^3.year

Figures 14 to 20 are real pictures of the ponds.

Figure 14: Picture of the covered pond.

Figure 15: Picture of the fan for the covered pond.

Figure 16: Picture of the side of the covered pond.

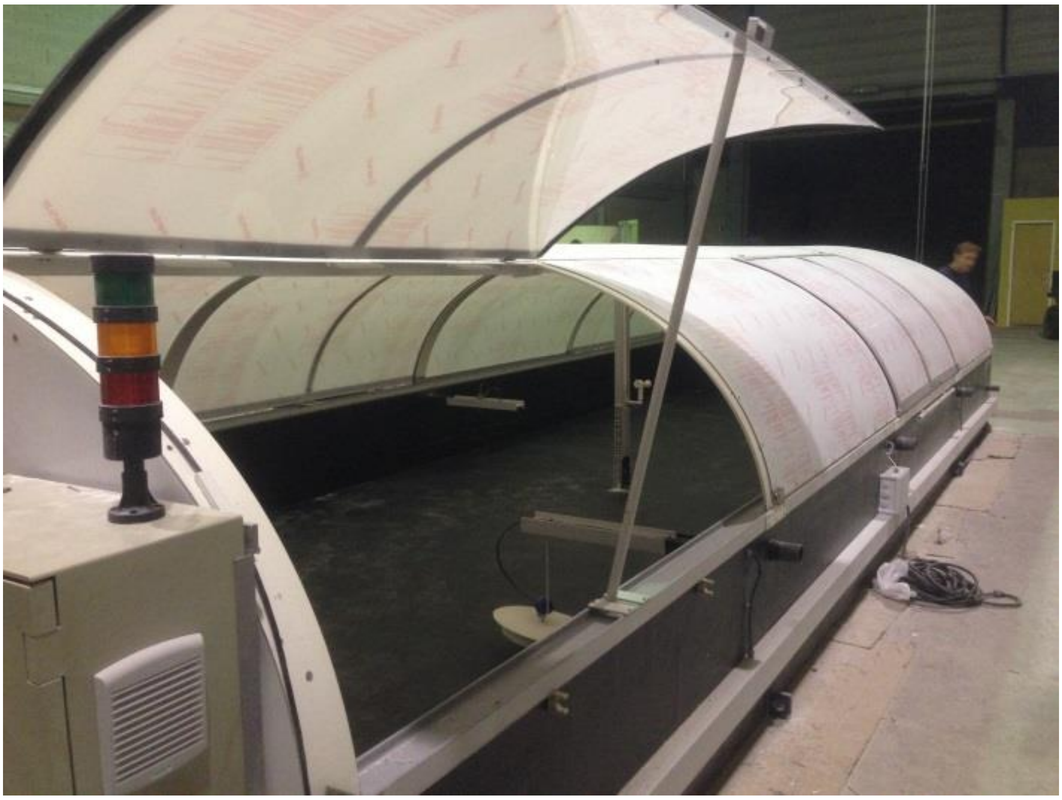

Figure 17: Picture of the covered pond while being constructed showing the side openings.

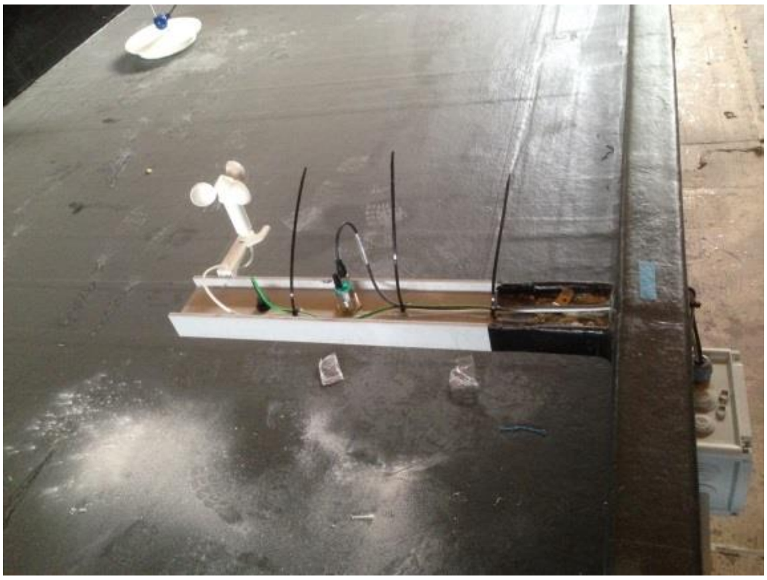

Figure 18: Picture of the sensors installed in the uncovered pond.

Figure 19: Picture of the open pond filled with water.

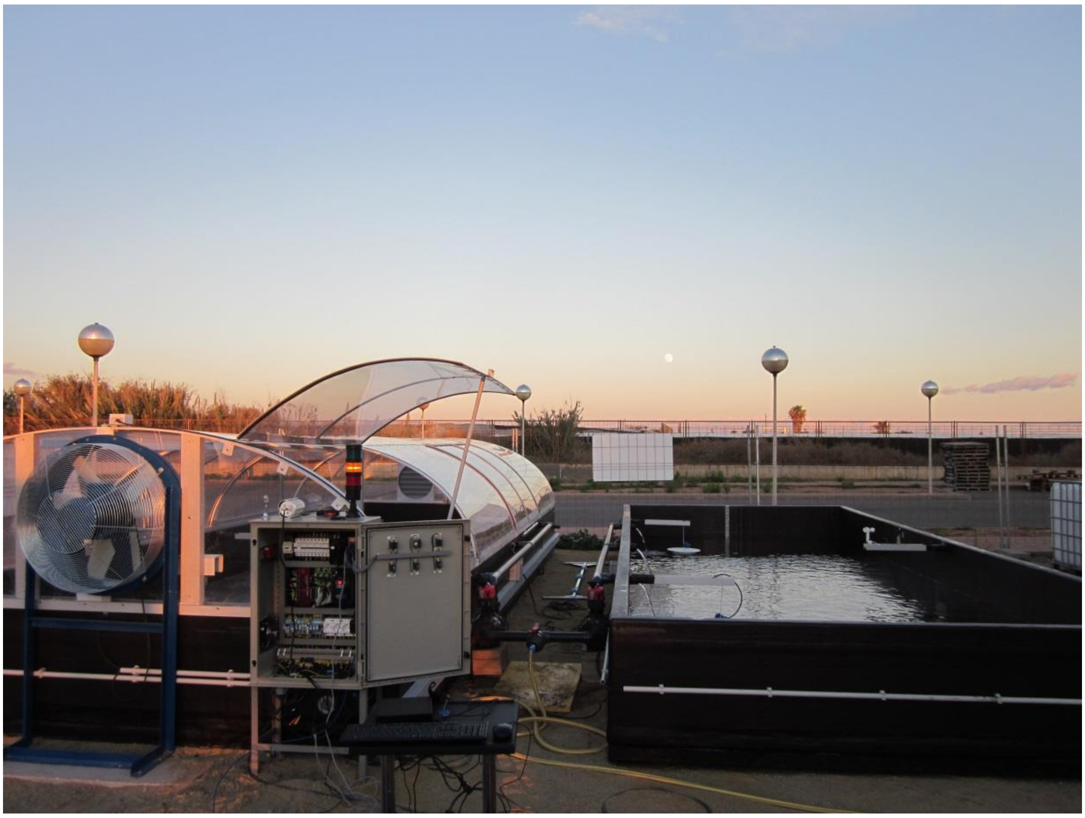

Figure 20: Picture of the two ponds working.

4 Solar Evaporation pilot plant

In this chapter will be reviewed some basic notions about heat transfer that will be important for the next chapters and then the pilot plant modeling will be presented.

4.1 Heat transfer theoretical background

Heat is the energy in transition between two points in space that have a temperature difference. When studying heat transfer we are studying how the energy is transferred in a heat form. This way one calculates the velocity at which the heat change occurs and the temperatures distribution in a substrate [30].

There are three mechanisms for heat transfer: conduction, convection and radiation, as summarized in the next sections.

4.1.1 Conduction

This type of mechanism only occurs in solids and fluids and is based in the energy transfer between molecules or atoms that collide with each other. There's a law that is used to calculate the heat transfer through this mechanism: the Fourier Law, which is described in Equation 1 [30].

$$Q = -k.A.\frac{dT}{dx}$$ **Equation 1**

where the variables have the following meaning:

Q – Heat flow, W/m^2

k – Thermal conductivity, W/m.ºK

A – Area of the heat transfer, m^2

$\frac{dT}{dx}$ – Temperature gradient, K/m

x – distance, m

4.1.2 Natural and forced convection

The convection type has two different mechanisms. The first one concerns the movement of macroscopic pieces of fluid, which means, molecules moving all together from a part of the fluid to another. The other mechanism is about individual molecules colliding with each other inside the fluid or against a solid surface in contact with the fluid. There are two types of convection: natural and forced [30] [32].

Natural convection occurs when there's no global movement of the fluid, or the movement is irrelevant, but there's a movement by parts of the fluid because of the difference of densities that comes from the different temperatures [30] [32].

Forced convection is when the fluid moves due to an outside action like a pump, the wind or a fan.

Equation 2 – Newton Law - is the model for the heat transfer by convection in which T_s is the temperature of the surface (ºC), T_∞ is the temperature of the fluid far from the surface (ºC) and h is the convection heat transfer coefficient (W/m2.ºK) [30] [32].

$$Q = h.A.(T_s - T_\infty) \qquad \textbf{Equation 2}$$

4.1.3 Radiation

A substance emits radiation in the form of electromagnetic waves when there is variation in the electron configuration of the atoms or molecules. The radiation goes through everything, including the void. The Equation that describes the heat transfer by radiation is the Stefan – Boltzmann Law [30] [32]:

$$Q_{emi} = \varepsilon.\sigma.A.T_s^4 \qquad \textbf{Equation 3}$$

where: ε – Emissivity (between 0 and 1); σ – Stefan Boltzmann constant = 5.6703×10^{-8} $W/m^2.K^4$

4.1.4 Combined heat transfer exercice

In order to understand better the heat transfer mechanisms, in Figure 21 there's an example of a heat transfer problem that is solved by a Matlab code using the main equations of heat transfer (Equatons 1, 2 and 3). In this example one considers the existence of two walls separated by 2 meters with air between them and the objective is to find the values of T_{1o} and T_{1i} after a year.

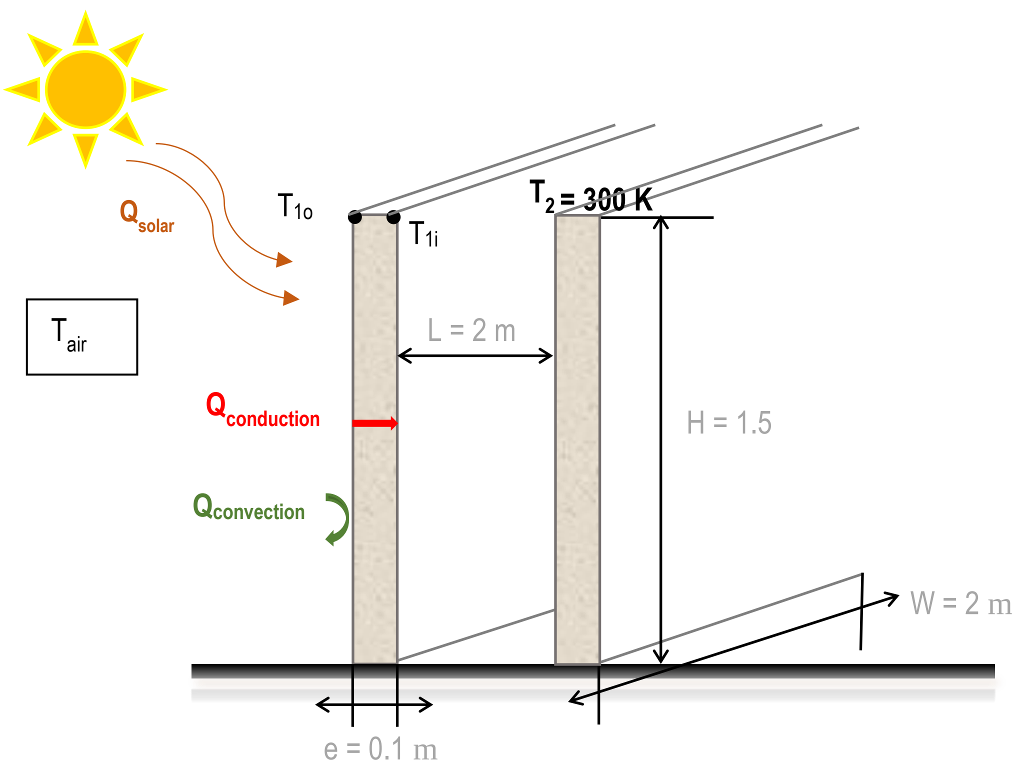

Figure 21: Sketch of the problem being studied.

To find out those temperatures the MATLAB program was used where were written all the variables and equations needed to calculate the variables wanted: T_{1o} and T_{1i}.

Next are represented the equations used in this example.

From Equation 3 is possible to writte Equation 4 and Equation 5 is the sum of Equations 1, 2 and 3.

Equation 6 is the convection heat transfer Equation in order to the temperature.

$$h_r = \varepsilon\sigma(T_2^2 + T_{1i}^2)(T_2 + T_{1i})A, \text{ with } \varepsilon = 1 \qquad \textbf{Equation 4}$$

$$Q = \frac{T_2 - T_{air}}{\frac{1}{h_c} + \frac{e}{k_1} + \frac{1}{h_r + \frac{k_{air}}{L}}} \qquad \textbf{Equation 5}$$

$$T_{1o\_new} = \frac{Q}{h_c A} + T_{air} \text{ and } T_{1i_{new}=\frac{Q\times e}{k_1\times A}+T_{1o\_new}} \qquad \textbf{Equation 6}$$

$$erro(T_{1i}) = \frac{T_{1i\_new} - T_{1i}}{T_{1i}}\ ;\ erro(T_{1o}) = \frac{T_{1o\_new} - T_{1o}}{T_{1o}} \qquad \textbf{Equation 7}$$

where:

ε – Emissivity (between 0 and 1)

σ – Stefan – Boltzmann constant, $W/m^2.K^4$

A – Area, m^2

e – Thickness of the wall, m

h_c – convection heat transfer coefficient, $W/m^2.ºK$

h_r – radiation heat transfer coefficient, $W/m^2.ºK$

k_1 – thermal conductivity of the wall, W/m.K

k_{air} – conductivity of the air, W/m.K

L – Distance between walls, m

Q – Heat transfer, W

T_2 – Temperature in second wall, K

T_{air} – Temperature of the air, K (data already storaged from a city in Spain with values for a year)

In order to calculate those variables an iterative procedure was used in which, first were given values to T_{1o} and T_{1i}, and those values were used in Equation 4. With the value of h_r, the value of Q was obtained (Equation 5) and with those values, T1o_new and T1i_new were calculated (Equation 6). If the error between T_1o and T_1o_new and the error between T_1i and T_1i_new

was below a certain value the interaction would stop, otherwise the iterative procedure should continue till the error value is achieved. The MATLAB code used is included in ANNEX II.
Table 13 contains all the values for the parameters used in this example.

Table 13: Parameters and values of the variables and of the results.

Parameter	**Value**	Units
Time	8760	Hour
h_c	5	W/m^2.K
k_1	0.2	W/m.K
k_{air}	0.0219	W/m.ºK
T1i_new	75.53	ºC
T1o_new	24.94	ºC

Analysing Table 13 it's possible to see that the exercise was for a year of iterations and the final values obtained for the wanted temperatures were 75.53 ºC for T1i_new and 24.94 ºC for T1o_new.
Figure 22 represents the results regarding the temperatures for a complete year of iteractions.

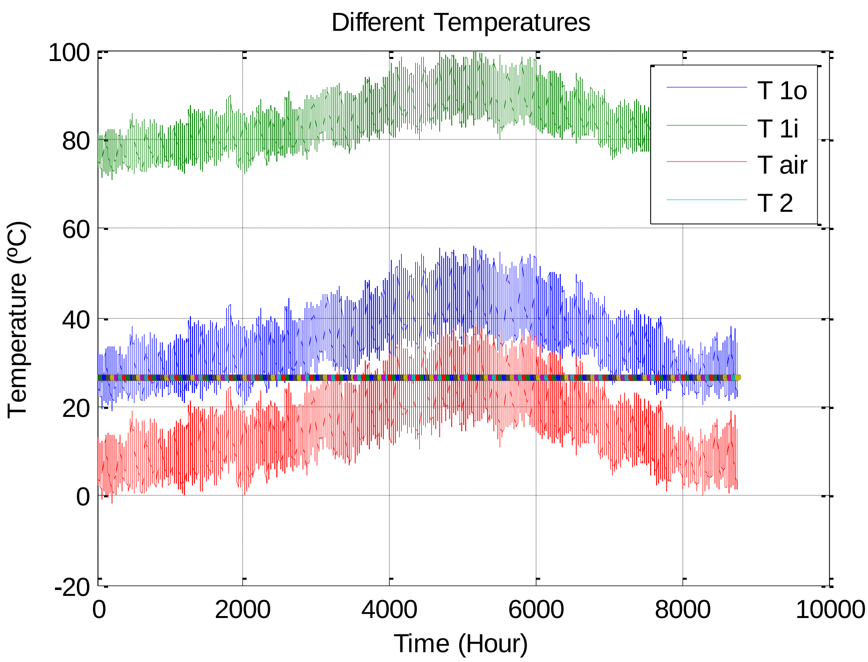

Figure 22: All the temperatures for a year of simulation.

In the last Figure it's possible to see how the temperatures vary over the year except T_2 that is always constant at 26.85 ºC (300 K).

4.2 Advanced Solar Evaporator simulation model

4.2.1 Theoretical background

The models (Model 1 and 2) used in developing this thesis are based on the article: advanced solar dryer for salt recovery from brine effluent of desalination MED plant [31].

The project of the article is called AQUASOL-enhanced Zero Discharge Seawater Desalination using Hybrid Solar Technology and the objective is to promote the use of solar energy in the desalination process and in the effluent treatment to improve the energy and environmental performance to make the MED desalination technology less expensive [31].

This decreasing cost will be obtained by associating the lower energy consumption in the MED process with the exploitation of sodium chloride that is obtained as sub product for the brine treatment.

In a solar saltwork the evaporation occurs in a natural way and it depends on several characteristics of the atmosphere, like air temperature and velocity, moisture and solar irradiation. The brine conditions are also importante [31].

When evaporating the water from the brine the salts start to precipitate from the least soluble ($CaCO_3$, $CaSO_4$) and occurs the production of NaCl (Sodium Chloride), Mg (Magnesium) and K (Potassium) salts (KCl, $MgSO_x$, $MgCl_x$) [31].

The extraction of the NaCl happens when submiting the brine to flow through a series of connected evaporation ponds.

To measure the concentration of salt produced it's used the Baumé scale (ºBe) (Equation 8), only used for fluids heavier than water at 15,5 ºC.

$$specific\ density = 145/(145 - {}^{\circ}Be) \qquad \textbf{Equation 8}$$

The evaporation has five distinct stages, the first three are called evaporators, the fourth stage is called the heater and the last one is where the NaCl is obtained and it's called the crystallizer.

In the first stage there's none salt precipitation and occurs the brine volume reduction. In the second one is visible the precipitation of about 55% of the $CaCO_3$ and of all the iron oxides. Calcium sulfate starts to precipate at stage 3 and at this stage all of de $CaCO_3$ has been precipitated.

In the heaters of fourth stage, continues the precipitation of $CaSO_4$ and in the final stage continues the same precipitaion and also the precipitation of Mg salts and sodium bromide [31].

It is importante to refer that along these stages the initial brine volume is being reduced [31].

In this paper (AQUASOL) was adopted a mathematical model and used Equation 9 as the representation of the energy balance (Figure 23).

$$d\rho_{brine}C_{pbrine}\frac{(T_{brine}-T_{initialbrine})}{\Delta t}=F_sH_h-q_e-q_c-q_r-q_b$$ **Equation 9**

where:

ρ_{brine} – Density of the brine, kg/m^3

F_s – Fraction of the solar energy absorbed by the brine layer.

H_h – Global irradiation in the horizontal plane.

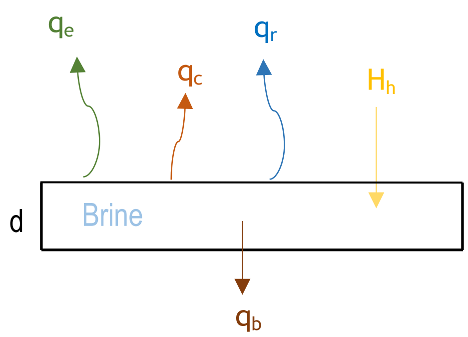

Figure 23: Energy Balance of a brine layer [31].

In which:

d – depth, m

H_h – Global irradiation in the horizontal plane.

q_b – Conduction heat transfer, W/m^2

q_c – Convection heat transfer, W/m^2

q_e – Evaporation heat transfer, W/m^2

q_r – Radiation heat transfer, W/m^2

The follow equations represent the convection losses (10, 11), the evaporation losses (12), radiactive losses (13) and conduction losses to the soil (14).

$$q_c=h_c(T_{brine}-T_{air})$$ **Equation 10**

$$h_c=2.8+3.0v$$ **Equation 11**

h_c – coefficient adopted for the calculation of the convection losses, W/m^2.ºC

v – air flow velocity, m/s

$$q_e = 0.0163h_c(P_{s,Tbrine} - \emptyset P_{s,Tair})$$ **Equation 12**

$$q_r = \varepsilon\sigma(T_{brine}^4 - T_{sky}^4)$$ **Equation 13**

$$q_b = \frac{K}{l}(T_{brine} - T_{soil})$$ **Equation 14**

where:

ε – Emissivity (between 0 and 1)

σ – Stefan-Boltzmann constant, $W/m^2.K^4$

hc – convection heat transfer coefficient, $W/m^2.ºK$

K – Soil conductivity, W/m.ºC

l – Total thickness, m

$P_{s,Tbrine}$ – Saturation pressure at brine temperature, Pa

$P_{s,Tair}$ - Saturation pressure at air temperature, Pa

q_b – Conduction heat transfer, W/m^2

q_c – Convection heat transfer, W/m^2

q_e – Evaporation heat transfer, W/m^2

q_r – Radiation heat transfer, W/m^2

T_{air} – Temperature of the air, K

T_{brine} – Temperature of the brine, K

T_{sky} – Temperature of the sky, K

T_{soil} – Temperature of the soil, K

v – Air flow velocity, m/s

Ø - Values of the relative humidity (obtained directly from the ponds)

Using all these equations it is possible to calculate the mass of evaporated water (kg/m^2) by using equation 15.

$$m = \frac{q_e \Delta t}{C_l} C_{evap}$$ **Equation 15**

In which:

C_l – vaporization latent heat

C_{evap} – evaporation coeficiente depending on the brine saline concentration and referred to distilled after evaporation, assuming values under 1.

These were the equations in which the model written was based on and it will be demonstrated more forward.

To put the model with all the conditions needed to test the ponds, the variables from Equations 10 to 14 were all substituted with real values obtained from the data from the ponds.

For exemple, the 'v' in Equation 11 is the velocity of the natural wind and the values come from the sensors in the pond.

The temperature of the brine is obtained by the natural temperature in the ponds measured with the sensors.

5 Experimental part

5.1 Data acquisition

Two codes were written (Model 2): one for the uncovered pond (natural convection) and another for the covered pond (forced air convection).

These codes were based in the equations represented in the AQUASOL project. In this case, Model 2, is the same as in AQUASOL project (Equations 8-15).

The ponds are eqquiped with sensors to read temperature, humidity, wind velocity and radiation, so the data used was obtained from there. The data used is only from 26th November 2015 till 28th January 2016 (two months).

Due to the timing of the project it wasn't possible to perform the study during the most favorable evaporation season so in these two months the analysis was performed in the lowest performance expected season.

Before the calculations there was a data treatment, which means that the data first of all was smoothed and then the data frequency was resized to fewer points spaced regularly along time.

For the natural convection were used equations 10 and 11 in which the values of the T_{brine}, T_{air} and v were obtained from the real data from the ponds. The same ocurred for equations 12, 13 and 14: the equations are the same and the data was obtained directly from the ponds.

The objective is to compare the level of the water and the mass of water evaporated between the two ponds.

In Figure 24 it's possible to see the level of the water in the open pond along the two months of analysis with real values obtained from the uncovered pond. The x label refers to the number of points recorded during the two months so, in this Figure are represented the depth points along time.

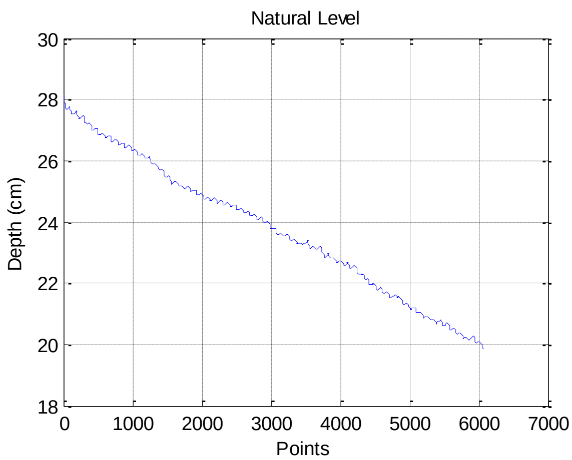

Figure 24: Depth of the uncovered pond with real data (Model 2).

In Figure 24 the maximum point is 28.13 cm and the minimum point is 19.86 cm. With this it's possible to conclude that the water level decreased 8.27 cm, which means this is the value that was evaporated in the two months of data acquisition.

In Figure 25 it's possible to see the variation of the calculated mass of water evaporated in the uncovered pond along the two months of analysis.

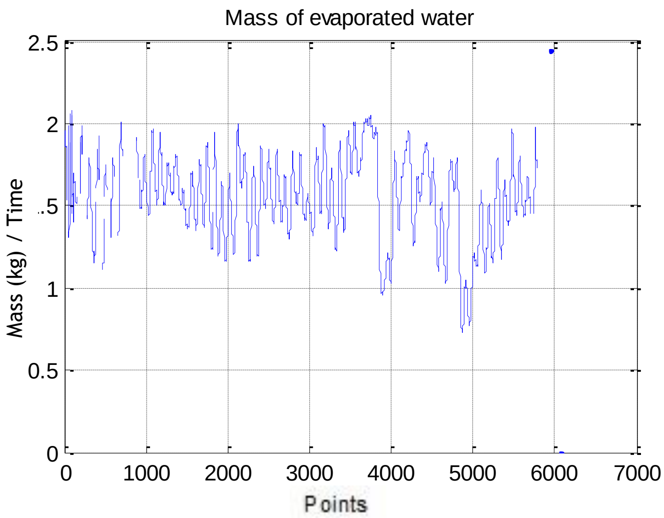

Figure 25: Mass of evaporated water for the uncovered pond (Model 2).

Analysing Figure 25 it's possible to see that the mass of water evaporated in the two months is always between about 1 and 2 kg everytime the depth decreased.

In figure 26 it is possible to see the depth evolution of the covered pond.

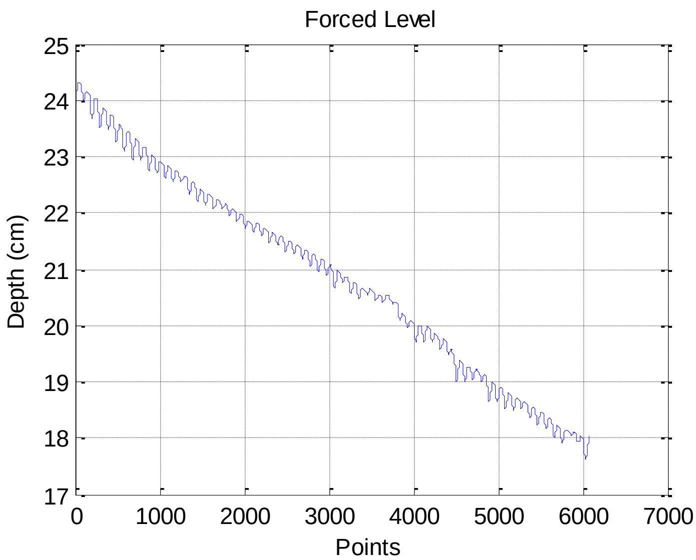

Figure 26: Depth of the covered pond (Model 2).

Analysing Figure 26 it is possible to conlude that the level of the water decreased from 24.32 cm to 17.63 cm, which means it lost about 6.70 cm of water: less than in the uncovered pond.
The covered pond evaporating less than the uncovered pond is not an expected result because the covered pond should work like a greenhouse with higher temperatures.
Due to the time available, the code wasn't finished and because of that will not be compared and will not be used to obtained the perfect regression Equation for the heat transfer.

5.1.1 Comparing the models

For comparing the models, in Model 1 all the meterological variables were replaced with the meteorological data from the ponds and the conditions were changed with the real conditions of the uncovered pond (area, daily production, thermal conductivity, heat transfer coefficients, etc). Figure 27 represents the depth in the natural pond using Model 1.

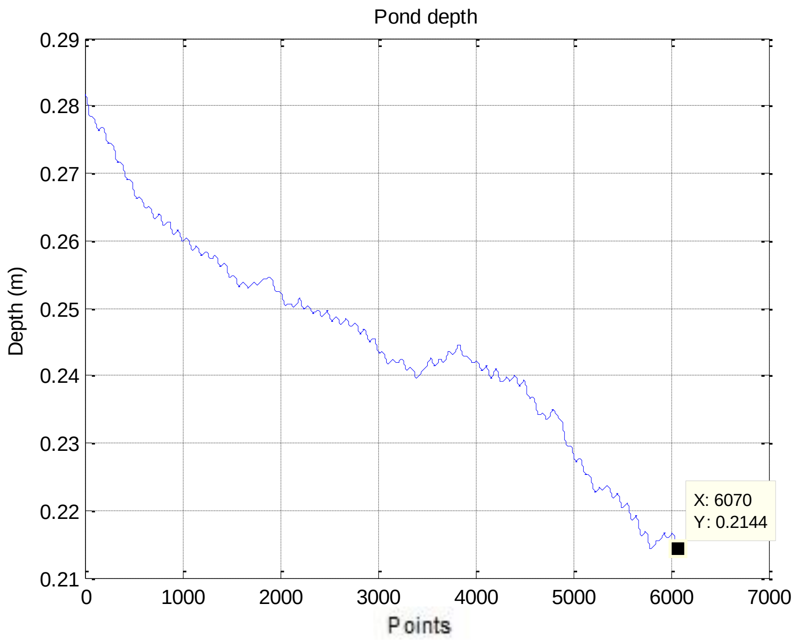

Figure 27: Natural Level with the simulations model (Model 1).

After anlysing Figure 27 and by comparing with the results from Figure 24 the conclusion is that the results are not so different. With the first model the depth decreased 8.27 cm and in this case the depth decreased 6.73 cm, about 20% different.

5.2 Model fitting

After getting all the data and all the models working this is the part where the coefficients are obtained (h_e and h_c). Another model was written (Model 3) and to calculate the coefficients Equations 10 to 14 were used.

First, it is possible to associate two of the heat coefficients by Equation 16:

$$\omega h_c = h_e \qquad \textbf{Equation 16}$$

where ω is a constant that will be calculated and:

h_c – convection heat transfer coefficient, W/m^2.ºC

h_e – evaporation heat transfer coefficient, W/m^2.ºC

From Equation 9 it's possible to call the variables in the the right side - Q_a:

$$d\rho C_p \frac{\Delta T}{\Delta t} = Q_a \qquad \textbf{Equation 17}$$

And replacing Equation 17 in Equation 9:

$$-Q_a + F_s H_s - q_e - q_r - q_b = q_c \qquad \textbf{Equation 18}$$

With the Equation 15 used to calculate the mass of water evaporated:

$$m_{evap} = \Delta d\rho = \frac{q_e}{C_l}.C_{evap}.\Delta t \rightarrow q_e = \frac{\Delta d\rho C_l}{C_{evap}\Delta t} \qquad \textbf{Equation 19}$$

With Model 3 was made a regression with some of the variables to relate all the points in order to obtain our own model. The Equation obtained is Equation 20 with a coefficient of determination (R^2) of 0.7.

The value of the coefficient of determination should be bigger than 0.9 to make sure that the regression is perfect but 0.7 was the best obtained and it proves that is a good regression.

The original format for the Equation obtained from the regresion is:

$$q_e = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_1 x_4 + \beta_5 x_2 x_3 \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 x_3 x_4 + \beta_8 x_1^2 + \beta_9 x_2^2 + \beta_{10} x_3^2 + \beta_{11} x_4^2$$

Analysing all the beta (β) values some of them were cut off because they were nearly zero. So after cutting off all the variables Equation 20 was obtained.

The variables used and their meaning, and the values of coefficients β are represented in tables 14 and 15, respectively.

$$q_e = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 x_2^2 + \beta_8 x_3^2$$ **Equation 20**

Table 14: Variables used in Equation 20 and their meaning.

x_1	x_2	x_3	x_4
Pressure difference (ΔP)	Temperature of the brine (T_b)	Air Temperature (T_{air})	Outside Radiation (OutRad)

In Table 14, all the values are obtained from the ponds measured by the sensors.
The values of x_2 and x_3, for exemple, are the values used in the calculation of the q_c (Equation 10).
x_1 is used in Equation 12 to calculate q_e.

Table 15: Values for the β coefficients in the Equation 20.

β_0	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_8
10.6703	-8.2103	-14.4062	-8.0319	19.8506	-13.0358	-30.2846	14.1762	32.2475

The same kind of regression was made to find out the qc, obtaining Equation 21.

$$q_c = \beta_1 x_1 + \beta_2 x_2$$ **Equation 21**

β_1 = 6,4911

β_2 = 0,9400

x_1= q_e

x_2= Outside radiation (data from the ponds)

With Equation 20 and Equation 21 is now possible to predict the behaviour of the ponds.
Knowing the variables needed in the equations it's possible to calculate the convection heat transfer and the evaporation heat transfer in the pond.
After making the regressions for the remain heat transfer like qb and qr is possible to calculate the amount of water evaporated by the energy balance in Equation 9:

$$d\rho_{brine} C_{pbrine} \frac{(T_{brine} - T_{initialbrine})}{\Delta t} = F_s H_h - q_e - q_c - q_r - q_b <=>$$

$$<=> \ d = \frac{F_s H_h - q_e - q_c - q_r - q_b}{\rho_{brine} C_{pbrine} \frac{(T_{brine} - T_{initialbrine})}{\Delta t}}$$

6 Proposals for further development

After studying the Matlab models and the ponds behaviour it's possible to make some notes on what should be improved to get better results.

The most importante thing is to make the study for a minimum of one year to see the behaviour over the four seasons. As mentioned before, this two months of study weren't during the best season.

Another important thing is to finish the matlab code for the covered pond in order to see how it works and improve it, if necessary, to obtain the best results and the equations to predict the evaporation behaviour inside it.

It is also important to compare it with the uncovered pond to see which one is better but the expectation is that the covered pond will be a best option because it creats a greenhouse effect, so the temperatures are higher and mass of evaporated water should be higher too.

Is importante to mention that the covered pond also has a part that recovers water from condensation that can be recovered as potable water for human use.

After modeling and optimization the ponds will be ready to use and then will be tested to see how they work with the seawater and with salts recovery.

If the ponds work as expected, later they can be used to test how they work for another kind of wastewater treatment instead of seawater desalination. For exemple, probably they can be used to treat olive mil wastewater which is a difficult task because of all the oil that is released: all the water is evaporated and then the olive oil can probably be reused for different purposes.

7 Conclusions

In order to try to solve the world's water scarcity, deslination tecnologies are being studied and improved.

This thesis studies the solar evaporation of the brine that comes from RO and EDM processes that are studied in the Zelda project.

To study the solar evaporation process, two ponds were built: one covered and the other uncovered.

The tests were written in Matlab based on heat and mass transfer phenomena based on another project, the AQUASOL.

The first model (Model 1) was developed by the CTM team with the restritions and caracteristics of the ponds and the second model (Model 2) is the same as in the AQUASOL project.

With the data obtained from the ponds, during two months, both models were compared to see if the behaviour was similar, it was found out that: in both ponds the evaporation predicted by both models was basically the same.

According to the model predictions, the uncovered pond was working perfectly and evaporating a reasonable amount of water during the two months of experience but the covered pond wasn't studied due the time that wasn't enough to finish the Matlab code.

After testing the similar behaviour between the variables used to calculate the heat transfer were made regressions with the variables and two new heat transfer equations for convection and evaporation were obtained (Model 3).

Calculate the rest of the terms of Equation 1 and finally calculate the depth variation from Equation 6.

With the convection and evaporation equations obtined it is possible to calculate the heat transfer coefficient for both and the amount of water mass evaporated.

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ANNEX I – Ponds control unit

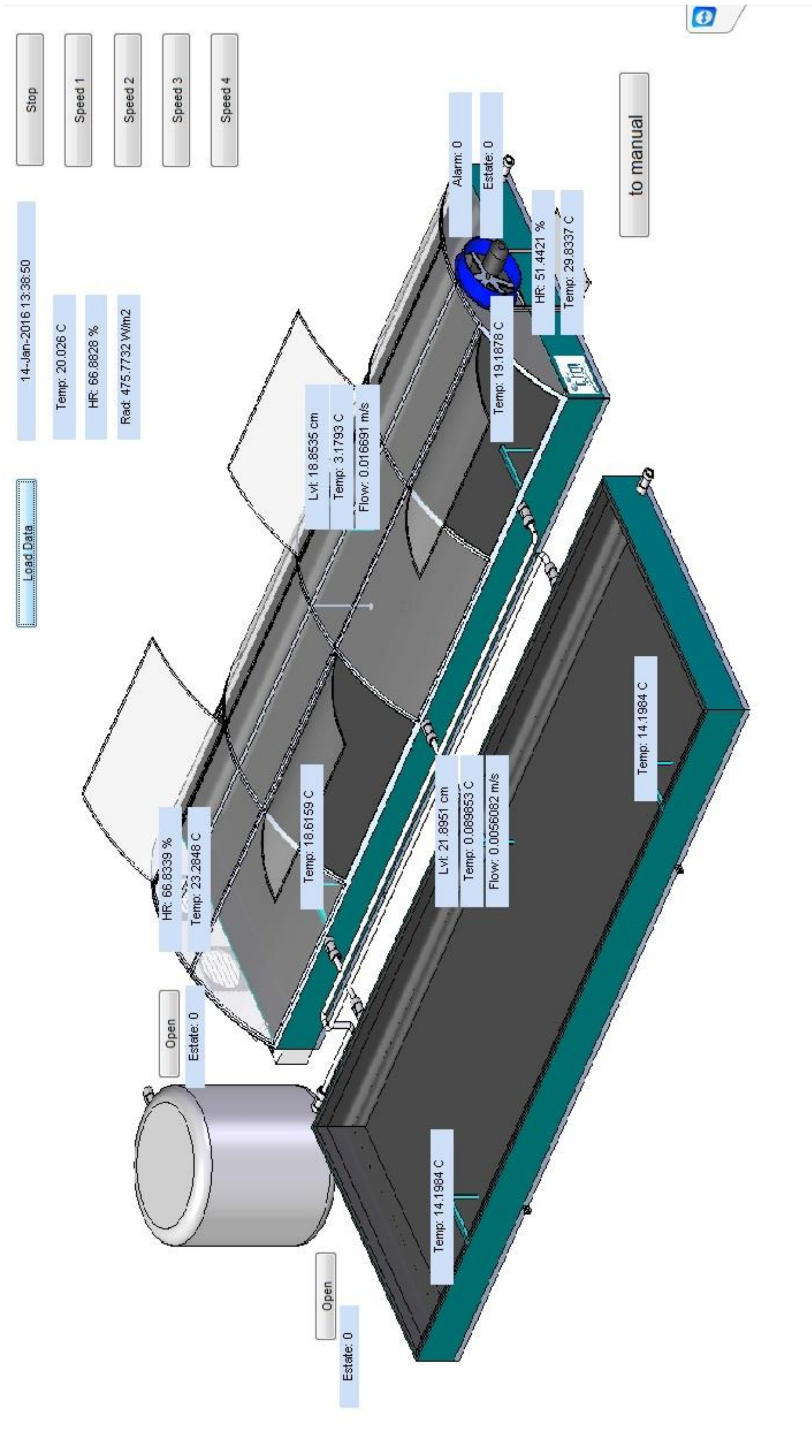

Figure 28: Picture of the monitor used to control the ponds.

ANNEX II – Matlab code of the exemple

```
clear; clc;
Meteo = importdata('meteo_files\ZonaC3.csv',';',2);
T_air = Meteo.data(:,4) + 273.15;
rad_normal = Meteo.data(:,8);
Anys = 1;
final_hour = size (T_air, 1);
T_2=zeros (final_hour, 1) + 300;
h_c=5;
k1=2;
e1=0.1;
L=2;
W=2;
H=1.5;
A=W*H;
k_air=100;
const_boltz = 5.67e-8;
Epsilon = 1;
T_1i (1) = 300;
T_1o (1) = 320;
max_error = 1e-03;
e = max_error+1;
fr = 1.0;
iteration=0;
time(1)=1;
for h=1:final_hour
time(h+1)=h;
while e > max_error
   h_r = epsilon*const_boltz*((T_2 (h) ^2 + T_1i (h) ^2)*(T_2 (h)-T_1i (h)));
   U = ((1/h_c)+(e1/k1))+(1/(h_r+(k_air/L)));
   Qs = rad_normal (h);
   Q = ((T_2 (h)-T_air (h)) + (Qs/h_c))/U;
   T_1o_new = (Q / (h_c)) + T_air (h);
```

```
    T_1i_new = ((Q*e1) / (k1)) + T_1o_new;
    e_T_1i = abs ((T_1i_new-T_1i (h))/T_1i (h));
    e_T_1o = abs((T_1o_new-T_1o (h))/T_1o (h));
    e = max(e_T_1i,e_T_1o);
    T_1i (h) = fr * (T_1i_new-T_1i (h)) + T_1i (h);
    T_1o (h) = fr * ( T_1o_new-T_1o (h))+T_1o (h);
iteration = iteration+1;
End
disp(['Hour= ',num2str(h),' iteration n= ',num2str(iteration),' Error= ',num2str(e)]);
e = max_error+1;
iteration = 1;
T_1i (h+1) = T_1i (h);
T_1o (h+1) = T_1o (h);
End
T_1o (end) = [ ];
T_1i (end) = [ ];
Time (end) = [ ];
```

ANNEX III – ZELDA

"The main objective of the ZELDA project is to demonstrate and disseminate the technical feasibility and economical sustainability of decreasing the overall environmental impact of desalination systems for freshwater production by adopting brine management strategies based on the use of electrodialysis metathesis (EDM) and valuable compound recovery processes with the final aim of reaching a zero liquid discharge (ZLD) process.

The first stage of the new process will have a clear demonstrative character and its main objective will be to prove the performance of the innovative EDM technology to highly concentrate the brines before entering the second stage of the process. The second stage of the new brine management process proposed in the ZELDA project has the final aim to achieve Zero Liquid Discharge (ZLD) desalination by means of recovery valuable compounds through precipitation, concentration and evaporation.

To demonstrate the environmental benefits of the new EDM-ZLD in the desalination brine treatment, a pilot plant has been constructed and will be installed and operated in the Almería, where brines from the RO-EDM treatment will be treated. The pilot plant constructed in the ZELDA project is divided in two steps: EDM and recovery of valuable compounds (ZLD).

The main result expected after the execution of the ZELDA project is to increase the sustainability of brackish water and seawater desalination systems for freshwater production, being some specific results the following ones:

- To design and construct a versatile brine treatment system based on EDM and recovery of valuable compounds.
- Performance and operational costs of the two stages of the process.
- To increase water recovery of the existing desalination plants.
- To decrease brine discharge into water bodies and, consequently, to reduce the environmental impact of current brine management strategies.
- To increase public awareness on the environmental impact of current brine discharge strategies.

The Life+ ZELDA project consortium consists on a Coordinating Beneficiary of the project, Fundació CTM Centre Tecnològic, and three associated beneficiaries: Fujifilm, Abengoa and European Water Supply and Sanitation Technology Platform.

The ZELDA project started on July of 2013.

Over the last decades, advances in desalination technology enabled obtaining freshwater from seawater or brackish water in regions with water scarcity. Although desalination technologies have a huge socio-economic positive impact, they also entail environmental drawbacks. Most of desalination plants use membranes to separate water from dissolved salts that are present in seawater or brackish water, thus leaving a highly saline solution named concentrate and also known as brine.

In case of seawater desalination, brine is usually discharged back into the sea. The whole scientific community agrees that brine discharge is a potential menace for marine ecosystem, generating environmental impacts in reception point such as diminishing the amount of flora and also creating salinity, temperature and alkalinity gradients. This impact is much more severe in case of brackish water desalination, when this concentrate is discharged into the surface or groundwater bodies because of higher salinity gradients.

The aim of LIFE+ ZELDA is to demonstrate the technical and economical feasibility of a new brine treatment system to reach zero liquid discharge (ZLD) desalination in both, seawater and brackish water desalination processes. Therefore, the main objective of the project will be to reduce the high environmental impact that nowadays brine discharge is causing in water ecosystems and increase the overall sustainability of desalination.

The innovative brine treatment system is based on electrodialysis metathesis (EDM) and recovery of valuable compounds (ZLD). In the EDM configuration, the sparingly soluble salts such as $CaSO_4$, $MgSO_4$ or $CaCO_3$, are not produced in neither of the concentrate streams. As a result, the brine can be more concentrated than in conventional electrodialysis (ED) process, increasing the overall recovery of desalination systems. In order to reach a ZLD desalination, and also to make the brine management more economically feasible, the EDM process will be coupled to a second stage aimed to recover valuable compounds. This second stage or ZLD stage involves controlled chemical reactions using non-hazardous chemicals. Depending on the chemical composition of EDM concentrates, the process will involve one or more precipitation routes combined with higher efficiency volume reduction technologies, such as brine concentrators. Furthermore to reach ZLD natural and intensive evaporation will be evaluated. It is expected that compounds such $CaCO_3$, $CaSO_4$, $Mg(OH)_2$, Na_2SO_4 and NaCl will be recovered.

To achieve ZELDA objectives, an EDM-ZLD pilot plant will be designed, constructed and implemented in the Almería SWDP. The technology will be evaluated and applied to treat different brines from Almería SWDP and from two BWDP, El Atabal and Helios. Furthermore the possibility of treat other brines will be considered.

In order to demonstrate overall environmental benefits and economical sustainability resulting from implementation of EDM-ZLD technology, results obtained during pilot plant operation will be analyzed using standardized and widely accepted Life Cycle Assessment (LCA) and Life Cycle

Cost (LCC) procedures and databases. Furthermore the overall sustainability of the proposed technology will be compared with brine discharge as well as the conventional processes for obtaining the recovered compounds, including mining activities.

Below there are listed the main results and environmental benefits expected after the execution of the LIFE+ ZELDA project:

- Versatile brine treatment system based on EDM-ZLD technology.
- Performance and operational costs of the new EDM-ZLD system to treat brines from both, seawater and brackish water desalination plants.
- The influence of the brine composition and operating conditions of the EDM-ZLD system on the overall sustainability of the desalination process.
- To increase the water recovery of the existing desalination plants.
- To decrease the brine discharge into water bodies.
- To decrease the environmental impact of obtaining valuable compounds recovered via conventional mining activities.
- To increase the public awareness on the environmental impact of current brine discharge strategies.

Moreover, the ZELDA project is completely in line with some of the most important policies and directives regarding water management at European level. The Water Framework Directive (WFD) (2000/60/EC) and the European Marine Strategy (EMS) (2008/56/EC) constitute the main legal framework at European level for the protection of aquatic systems. Brine discharge into water bodies, which is the most common option of current seawater and brackish water desalination plants, is in clear conflict with the objective of both, the WFD and the EMS. Furthermore, unfortunately, there is no specific legislation prohibiting the brine discharge.

With the results obtained in the ZELDA project, it is expected to demonstrate the high environmental gains of a Zero Liquid Discharge desalination compared with current brine management strategies, contributing to the implementation of new European legislation focused on brines.

Figure 29: Almería desalination plant.

Information about the Life+ ZELDA Project has also been published in the WssTP newsletter (October 2013), the CTM newsletter (December 2013), the CTM magazine (November 2013) and also in the ABENGOA webpage.

ZELDA project has also gained visibility through its participation at large European conferences as Water Innovation Europe 2014 and EIP Water Conference 2014.

It has been demonstrated at laboratory scale that the proposed new EDM-ZLD process is technically feasible, allowing achieve zero liquid discharge in water desalination. Furthermore, results obtained during the first half of the project allowed design and construct a pilot plant in order to validate the technical and economical viability of the EDM-ZLD implementation. The pilot plant was going to be installed at Almería on June 2015 (supposly) but was installed in November 2015, and during the following two years different brines will be treated. During pilot plant operation results will be more visible. It will be possible to consult real-time data from pilot plant in the ZELDA website demonstrating the technical feasibility of the EDM-ZLD process.

Brine management and disposal, especially for inland applications, is currently one of the most challenging issues associated with water desalination. The disposal of brine from desalination plants into water bodies conflicts with the objectives of the Water Framework Directive (2000/60/EC) and, therefore, it is necessary to implement brine management strategies that do not include its release into the environment.

ZELDA project will contribute on the accomplishment of WFD by developing a new process for brine treatment. The new EDM-ZLD process will allow achieving zero liquid discharge in seawater and brackish water desalination reducing its environmental impact and increasing the overall sustainability of desalination. So, the main environmental benefits associated to EDM-ZLD process are:

- Reducing the amount of brine discharged to the water bodies.
- Increase freshwater production in desalination processes.
- The new EDM-ZLD process will convert brine to a secondary source allowing the recovery of valuable compounds and reducing the natural resources consumption.
- Improve status of water bodies, not only the sea, also aquifers and rivers.
- Reduction of water scarcity.

Furthermore, the project ZELDA is clearly a climate change adaptation project.”

Table 16: List of Deliverables to be produced during the first half of the Project.

Deliverable	Status
Project Logo	✓
Main characteristics of Almería seawater	✓
Novel ion-exchange membranes characterization and performance	✓
P&I Diagram and main component description of the EDM stage	✓
Compound recovery strategies from seawater and brackish water brines	✓
P&I Diagram and main component description of the ZLD stage	✓
Fully automated EDM system with capacity of handling around 1 m3/h of brine	×
Zero Liquid Discharge stage of the pilot plant constructed	×
Project website completed	×

At the time this report was written the last three deliverables weren't finished and they were estimated to be finished in June 2015.

That finishing line wasn't fulfilled, they were all finished till November 2015.

Table 17: List of Milestones to be produced during the first half of the project

Milestone	Status
Nomination of the Project Manager and the Steering Comitee	✓
Best membrane configuration for EDM selected	✓
Project website activated	✓
Environmental and economical impact calculation methodology	✓

EDM-ZLD pilot plant continuosly operating in Almería seawater desalination plant ×

The EDM-ZLD pilot plant continuosly operating in Almería seawater desalination plant started to be operated in November 2015.